

Comparative Study on Sorption Additivity of Individual and Coexisting Cesium and Selenium on Bentonite/Quartz Sand Mixtures

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Abstract—This study focused on sorption of individual and coexisting Cs and Se on bentonite and quartz sand mixtures by batch techniques. Batch kinetic tests have been conducted with carrier free by using individual and coexisting radiotracers, ¹³⁷Cs and ⁷⁵Se. The distribution coefficients (K_d) of Cs on bentonite showed that there is no interference on sorption additivity between individual and coexisting value (366 ± 3 and 371 ± 10 mL/g in synthetic groundwater, 43 ± 1 and 60 ± 2 mL/g in synthetic seawater). Moreover, individual and coexisting K_d (22 ± 2 and 20 ± 4 mL/g in synthetic groundwater, 10 ± 1 and 14 ± 1 in synthetic seawater) of Se are in similar case with Cs. The experimental results also present in sorption of ¹³⁷Cs and ⁷⁵Se on bentonite/quartz sand mixtures (1:1). It is easily found that sorption mechanisms of Cs and Se on bentonite and quartz sand mixtures are independent and different by using radiotracer technique. According to different sorption mechanisms of Cs and Se, the sorption additivity by batch sorption experiments would be quite helpful while assessing buffer materials mixed by bentonite and quartz sand.

Keywords—Sorption; Individual; Coexisting; Cesium; Selenium

I. INTRODUCTION

There are three operating nuclear power plants in Taiwan. Another one is under construction and is expected to be put into operation in 2016. These plants will generate high-level nuclear waste (HLW) during operation. How to properly dispose the radioactive waste is an urgent topic in Taiwan. Since deep geological multiple-barrier repository has been widely accepted as an effective way to prevent and control the release of the nuclear waste, a deep geological disposal project in Taiwan was initiated several years ago.

Materials presenting high retention properties towards radionuclides in aqueous media are required in radioactive waste engineering and natural barriers are used to prevent the dispersion of radioactivity from repositories. Bentonite clay and quartz sand have been selected as potential buffer and backfill materials for HLW disposal [1]. The functional requirements of buffer materials consist of both engineering and chemical properties [2][3]. Bentonite was associated with high cation exchange capacity, high swelling potential and low hydraulic conductivity, while quartz sand was associated with high thermal conductivity and better mechanical properties.

There are two important radionuclides in high-level radiowaste including ¹³⁷Cs ($T_{1/2}=30.2$ years), ¹³⁴Cs ($T_{1/2}=2.4$ years), and ¹³⁵Cs ($T_{1/2}=2.3 \times 10^6$ years) for several reasons: they exhibit high water solubility, have long half-life, and Cs can be easily incorporated into terrestrial and aquatic organisms

(because of its chemical similarity to K [4]). Moreover, the bioavailability of Cs in natural systems depends on sorption properties of the solid phases. Therefore, sorption of Cs has been studied on many sorbents reflecting their properties for safety assessment.

Selenium, a member of Group VI of the Periodic Table (atomic number 34), has considerable chemical similarities to S, resembling the latter in many forms and compounds. Selenium is also a redox sensitive element and the amount of Se present in the diet may result in either deficient or toxic responses and it has been reported in previous literature [5]. In addition, ⁷⁹Se (2.95×10^5 years half-life) is a fission product in high-level radiowaste. According to pH-Eh diagram of Se, elementary selenium (Se^0) and selenide (HSe^-) should prevail in reducing conditions, selenite (SeO_3^{2-}) and selenate (SeO_4^{2-}) in oxidizing conditions. Under reducing conditions the solubility of selenium is theoretically controlled by the formation of metallic Se and in the presence of metallic cations (e.g. Fe^{2+}) also by the precipitation of the metallic-selenide salt (e.g. FeSe or FeSe_2) [6][7]. The assessment to what extent ⁷⁹Se is a critical radionuclide for the geological disposal of high-level radiowaste, depends on its actual speciation under storage conditions.

The radionuclide inventory in HLW and the true situation of repository are quite complicated. To provide accurate data for performance assessment of HLW repository, it is not enough just to study individual radionuclide's behavior in geological environment. It is also important to realize the reaction or migration of coexisting radionuclides in geological environment. Therefore, it is necessary to clarify the major mechanism of different radionuclides. Thus, batch techniques are frequently used to characterize the sorption of radionuclides in laboratories. Generally, the distribution ratio, R_d , or distribution coefficient, K_d , is applied to characterize materials to retard the transport of radionuclides in geological disposal. The R_d or K_d can be written as following in a mixture

$$K_d \text{ or } R_d \text{ (mL/g)} = \sum f_i \cdot R_{di} \quad (1)$$

where f_i is the mass fraction of mineral i in the mixture, and R_{di} is the distribution ratio of radionuclides on mineral i .

Sorption mechanism of Cs and Se has been reported in several studies by using ion-exchange [8]-[11] or surface-complexation models [12][13], respectively. It is found that the major ion-exchange factor of controlling Cs sorption is cation, especially Ca^{2+} and Na^+ . Moreover, it demonstrated that sorption mechanism of Se is related to iron

oxides in materials, especially goethite, hematite, or apatite et al. [14][15]. In fact, there are some studies about additivity rule of sorption behavior on soils and mixtures for radionuclides. Some studies have indicated that sorption of actinides (Np and Am) [16] on bentonite provide reasonable agreement with additivity rule, but some overestimate of K_d in Cs and Sr mixtures. The results demonstrated that it increased sorption additivity of Cs and Se in synthetic seawater with higher bentonite content in mixture [17]. Moreover, it is quite clear that sorption of Cs and Se on mudrock are independent because of different mechanisms [18].

This study focuses on sorption of Cs and Se on bentonite and quartz sand by using radiotracer's technique of individual and coexisting ^{137}Cs and ^{75}Se in order to realize if there is any sorption interference between Cs and Se in bentonite/quartz mixtures. Both synthetic groundwater (GW) and seawater (SW) were used in this work to take into account the extreme situations of highly reducing groundwater or the instruction of seawater into the repository.

II. EXPERIMENTS

A. Materials

The bentonite and quartz sand used in this investigation were purchased from the American Colloid Company type MX-80 (Wyoming Na-bentonite) and Taiwan San-I Mining Company, respectively. The bentonite (MX-80) has a clay content ($< 2 \mu\text{m}$) of approximately 85% and a montmorillonite content of 80–90 wt % of this fraction. Quartz sand with particle size from 0.297 to 0.84 mm used in this work has a high purity ($\sim 99.5\%$) of SiO_2 . The mineral and chemical compositions of bentonite were given in Table 1 and 2. Synthetic groundwater (GW) and seawater (SW) composition list in Table 3 was used in all experiments.

TABLE 1 MINERALOGICAL COMPOSITIONS OF BENTONITE (MX-80)

Mineral	Weight Content
Montmorillonite	80 ~ 84%
Quartz	6 ~ 7%
Phlogopite	2.5 ~ 4.3 %
Plagioclases	3.5%
Feldspars	1.2%
Calcite	1.6%
Pyrite	0.6%
CEC	76 Meq/100 g

TABLE 2 CHEMICAL COMPOSITION OF BENTONITE (MX-80) BY ICP-MS DIGESTION ANALYSIS

Element	Weigh Content
SiO_2	60.35
Al_2O_3	20.12
Fe_2O_3	3.14
MgO	2.65
CaO	0.44
K_2O	0.53
Na_2O	2.13
Others (anions)	10.66
Total	100.22

TABLE 3 THE COMPOSITIONS OF LIQUID PHASES USED IN THIS STUDY

Components	GW (M)	SW (M)
Cl^-	1.78E-01	5.50E-01
SO_4^{2-}	5.83E-03	2.81E-02
HCO_3^-	1.64E-04	—
F^-	8.00E-05	6.80E-05
Br^-	5.01E-04	8.39E-04
BO_3^-	—	4.16E-04
Ca^{2+}	4.72E-02	1.03E-02
Mg^{2+}	1.73E-03	5.31E-02
Na^+	9.13E-02	4.70E-01
K^+	2.07E-04	1.02E-02
Sr^{2+}	4.00E-04	8.70E-05
Li^+	1.44E-04	2.50E-05
pH	7.3 ± 0.2	6.8 ± 0.3
Eh (mV)	220 ± 5	230 ± 5
I (M)	~ 0.33	~ 1.22

B. Radiotracer Preparation and Identification

Radiotracer, ^{75}Se ($t_{1/2}=119 \text{ d}$), was applied in present work [18]. Moreover, the radiotracer, ^{137}Cs (γ -ray, $E = 661 \text{ keV}$) purchased from Amersham (U.S) was also added into stock solution (synthetic groundwater and seawater used in this study). Finally, 3mL stock solution of Cs and Se were individual and simultaneous analyzed at 2 energy ranges from 60- 467 keV and 500-700 keV by an auto-gamma NaI(Tl) counter (Packard 5002, USA). Before the batch test, 3 stock solutions were prepared for individual and coexisting Cs and Se, and recorded as initial radioactivity, respectively.

C. Batch Sorption Kinetic Test

ASTM batch tests were applied in this work [19]. There are 3 portions of the samples were prepared in centrifugal tubes (50 mL) in triplicate for individual and coexisting radionuclides (^{137}Cs , ^{75}Se , $^{137}\text{Cs}+^{75}\text{Se}$). The each stock solution contained trace amount of radiotracers, ^{137}Cs , ^{75}Se and $^{137}\text{Cs}+^{75}\text{Se}$, was also added to solution (GW and SW) prior to batch tests. Radiotracers of ^{137}Cs and ^{75}Se were employed to trace the concentration changes during sorption experiments. Batch tests were also conducted with a solid/liquid ratio of 1 g/30 mL in both conditions. After 1, 2, 4, 8, 12, 24, 48, 96, 168, and 336 hours of shaking, tubes were removed and centrifuged in rpm ($=10380 \text{ g}$, Kokusan H-200, Japan) for 5 minutes. In addition, its pH and Eh values were also measured by glass electrode (InoLab-412, Mettler Toledo, Swiss) and platinum glass electrode. The radioactivity in the supernatant solution was measured and determined the relative radioactivity of ^{75}Se and ^{137}Cs in the liquid phase (*i.e.*, cpm/mL). The chemical forms of radiotracers are $^{137}\text{CsCl}$ and $^{75}\text{SeO}_3^{2-}$. The distribution coefficient (K_d) was adopted by the following formula :

$$K_d = \frac{A_0 - A}{A} \cdot \frac{V}{M} \quad (2)$$

where A is the equilibrium radioactivity of radionuclides (cpm/mL), A_0 is the initial radioactivity of radionuclides in solution (cpm/mL), and V and M are liquid volume (mL) and solid mass (g).

III. RESULTS AND DISCUSSION

A. Sorption of Individual ^{137}Cs and ^{75}Se on MX-80 and Quartz Sand

Figure 1 showed that K_d of individual ^{137}Cs and ^{75}Se in GW and SW obtained by batch tests in 14 days. According to the previous studies [20][21], Cs sorption belongs to fast-uptake reaction and reaches equilibrium within 4 hours in Figure 1 (a). It also shows that results of batch tests indicated K_d ($\approx 366 \pm 3$ mL/g) for Cs in GW is higher than that ($\approx 43 \pm 1$ mL/g) in SW due to higher ion strength in SW. In addition, it demonstrates that the major influence on sorption of Cs in MX-80 is ion strength (I) and the principal mechanism controlling Cs sorption is ion exchange especially for Na^+ and Ca^{2+} ion [22]. Therefore, sorption of Cs in MX-80 decreases as ion strength increases due to higher ion's concentration in SW. Furthermore, sorption of Se belongs to slow-uptake reaction and reaches equilibrium within 4 days in Figure 1 (b). It also prevails the similar case to Cs that K_d ($\approx 22 \pm 2$ mL/g) for Se of GW is higher than that ($\approx 10 \pm 1$ mL/g) in SW. Therefore, K_d for Cs is larger than Se because of higher clay content in MX-80 contributing high ion-exchange capacity. Besides, Figure 2 showed that K_d ($\approx 1 \pm 0.5$ mL/g) of individual ^{137}Cs and ^{75}Se in GW and SW has a similar result of quartz sand. It is quite clear that there is no any sorption ability of Cs and Se on quartz sand.

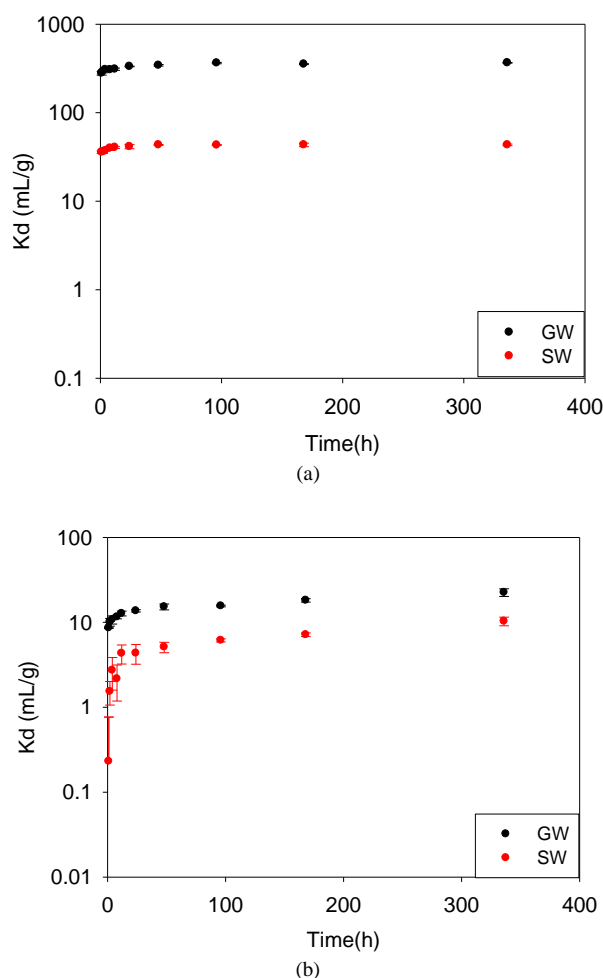


Fig. 1 Kinetic sorption of individual Cs and Se on MX-80 in GW and SW
(a) ^{137}Cs , (b) ^{75}Se

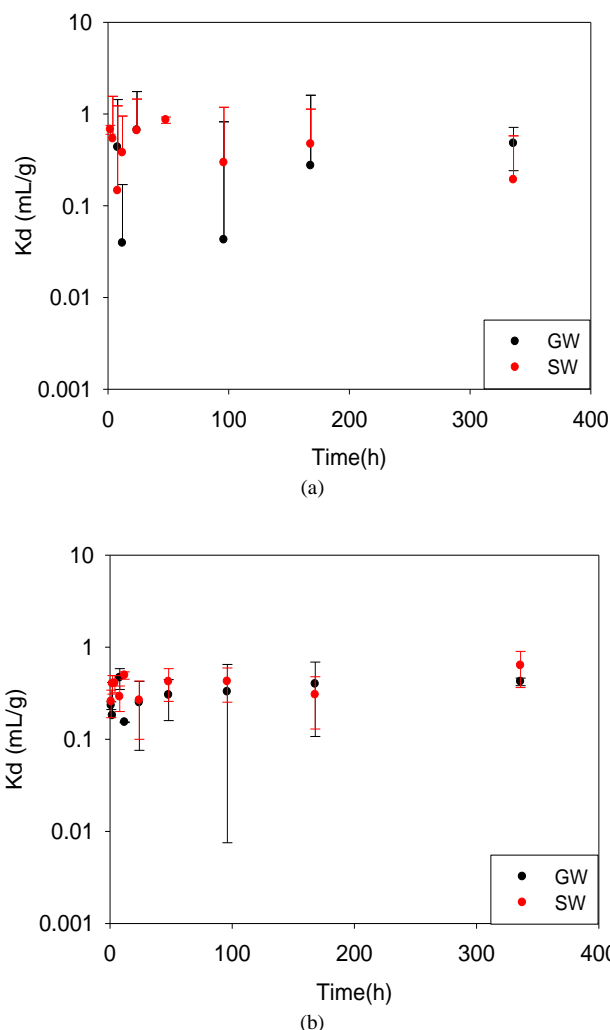


Fig. 2 Kinetic sorption of individual Cs and Se on quartz sand in GW and SW
(a) ^{137}Cs , (b) ^{75}Se

B. Sorption of Coexisting ^{137}Cs and ^{75}Se on MX-80 and Quartz Sand

Figure 3 (a) illustrates that K_d ($\approx 371 \pm 10$ and 60 ± 2 mL/g) of coexisting Cs (^{137}Cs & ^{75}Se) in GW and SW is in agreement with K_d of individual Cs. It demonstrates that the major factor on sorption of coexisting Cs and Se for Cs in MX-80 is ion strength (I) and sorption mechanism is ion exchange [23][24]. Therefore, sorption of Cs in MX-80 would not be affected by ^{75}Se . Moreover, Figure 3 (b) also displays that K_d ($\approx 20 \pm 4$ and 14 ± 1 mL/g) of coexisting Se (^{137}Cs & ^{75}Se) in GW and SW is equivalent to K_d of individual Se. Some literatures have stated that the main mechanism controlling Se sorption is surface complexation with iron oxides [25][26]. The results of Figure 3 could demonstrate that sorption mechanism of Cs is not only different from that of Se but also have no interfering effect with Se. Figure 4 also showed a result in agreement with Figure 2 no matter individual and coexisting Cs and Se on quartz sand.

C. Sorption of Individual and Coexisting ^{137}Cs and ^{75}Se on MX-80 and Quartz sand Mixtures (1:1)

Figure 5 demonstrated that K_d of individual and coexisting ^{137}Cs and ^{75}Se in GW and SW on MX-80 and quartz sand mixtures (1:1) obtained by batch tests in 14 days. Figure 5 (a) and (b) showed an approximate K_d ($\approx 300 \pm 5$ and 35 ± 1 mL/g)

in GW and SW of MX-80 and quartz sand mixtures (1:1). The same case of Se in Figure 5 (c) and (d) is in agreement with Cs that K_d ($\approx 20 \pm 2$ and 10 ± 1 mL/g) of individual and coexisting ^{137}Cs and ^{75}Se in GW and SW on MX-80 and quartz sand mixtures (1:1). From the results in Figure 5, it is found that sorption of Cs in MX-80 would be interfering with Se because of independent sorption mechanism

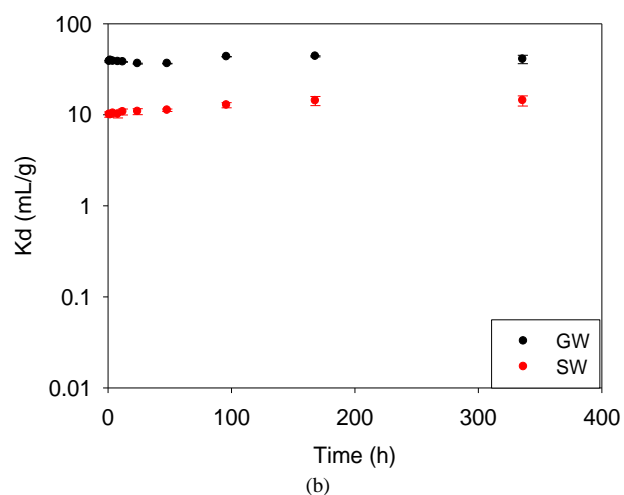
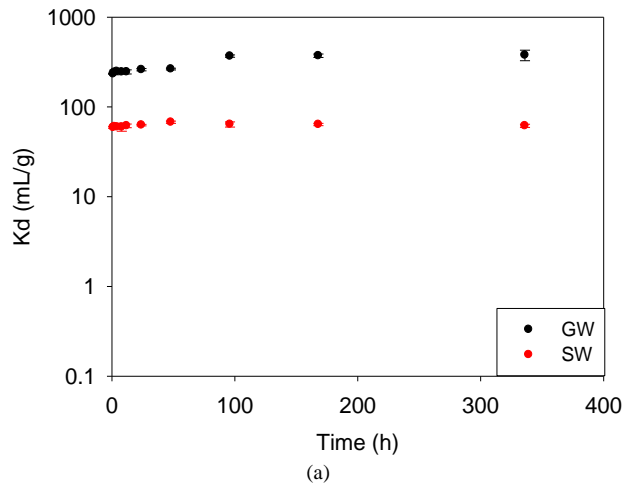


Fig. 3 Kinetic sorption of coexisting Cs and Se on MX-80 in GW and SW. (a) ^{137}Cs (Cs&Se), (b) ^{75}Se (Cs&Se)

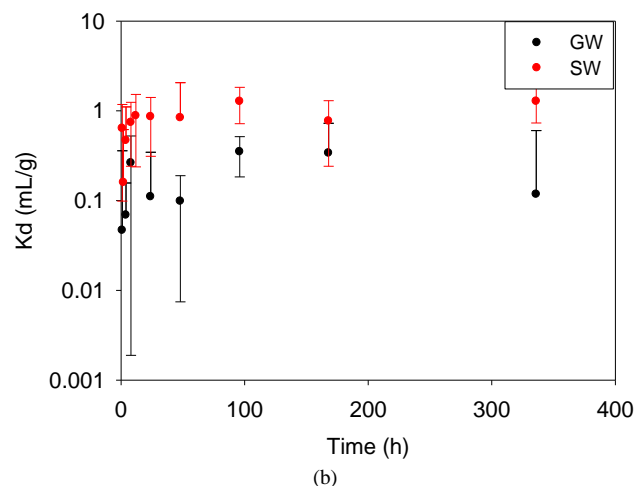
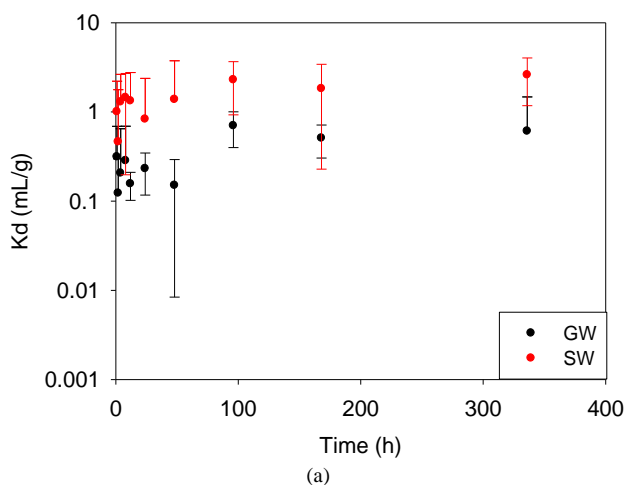


Fig. 4 Kinetic sorption of coexisting Cs and Se on quartz sand in GW and SW (a) ^{137}Cs (Cs&Se), (b) ^{75}Se (Cs&Se)

IV. CONCLUSION

In this study, the similar results of batch tests are also showed in previous work [18]. The both results indicated K_d value for individual and coexisting Cs and Se in Taiwan mudrock and MX-80/quartz mixtures didn't have an obvious difference. Moreover, K_d value of Cs is proportional to clay content in materials (MX-80 ~80% > Mudrock~40%), but higher ion strength (I) in liquid reduced it in both cases. Therefore, it further clarified that major sorption mechanism of Cs is ion exchange and ion strength (I) is the major factor that affects Cs sorption. Furthermore, sorption of Se is related to iron oxide's content in materials (Mudrock~5% > MX-80~3%) from the results of individual and coexisting Cs and Se. It is easy to find that K_d of Se on Mudrock is higher than that MX-80 because of different iron oxides. According to both works, it demonstrates further that sorption mechanisms of Cs and Se are quite different, and the sorption additivity by batch sorption experiments would be quite helpful while assessing buffer/backfill materials mixed by bentonite and quartz sand.

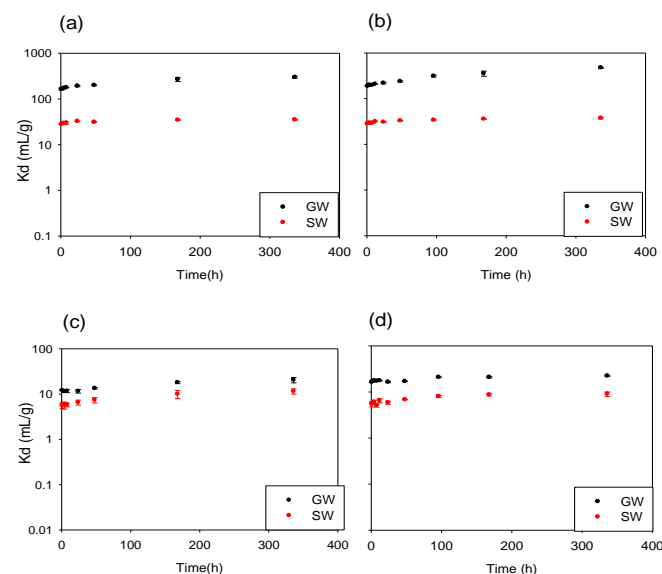


Fig. 5 Kinetic sorption of individual and coexisting Cs and Se on MX-80 and quartz sand mixture (1:1) in GW and SW. (a) ^{137}Cs , (b) ^{137}Cs (Cs&Se), (c) ^{75}Se , (d) ^{75}Se (Cs&Se)

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